

Poster Presentations

[MS22-P01] The Solid and Solution States Mysteries of Rhodium(I) Functionalized Tropolonato Complexes

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Crystal engineering is the planning and construction of the structure and properties of crystalline materials by designing molecular building blocks.¹ In this regard, tropolone (2-hydroxy-2,4,6-cycloheptatrienone) have been utilized as building blocks for the construction of liquid crystals and organogels.² The growing application of rhodium(I) tropolonato tertiary aryl phosphine complexes toward oxidative addition as relevant to the Monsanto process, has also gained significant interest since the work done by Steyl et al. in the early 2000's.^{3,4} The small bite (OM-O) angle in tropolonato rhodium(I) complexes make them suitable to accommodate two phosphine/arsine ligands in the rhodium coordination sphere, hence forming a trigonal-bipyramidal geometry.⁵

Moreover, tropolone ligands are symmetrical, thus, they are considered good for catalyst design. As a result, the isomerization of the oxidative addition products is irrelevant as observed for other rhodium complexes.⁶

In this study, the effect of functionalized tropolone toward oxidative addition of methyl iodide to the rhodium (I) metal centre was investigated. The more sterically hindered functionalized tropolone ligand (Figure I) was utilized to manipulate the rhodium metal centre.

To complete the coordination sphere of the rhodium (I) metal centre, tertiary aryl phosphine and carbonyls ligand moieties were used to design the precursors of the type $[\text{Rh}(\text{TropXn})(\text{CO})(\text{PR}_3)]$ ($\text{X} = \text{methylpiperazine, methyl(4-phenyl)piperazine}$), $\text{R} = \text{tertiary aryl phosphine}$, and $n = 2,3$). All materials and the resultant products were characterized in their solid state by single crystal x-ray diffraction. Solution state characterization was obtained by multinuclear NMR, infrared and UV-Vis spectroscopy. These techniques were vital in the characterization of the intermediates species formed during the oxidative addition, hence were useful in proposing the mechanism and the rate law suitable for the reactions. The mechanism of action in the iodomethane oxidative addition will be discussed in detail in this presentation.

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